

AUGMENTATION OF THE PROCESSES

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COMPOSITION, STRUCTURE, AND PROPERTIES OF OXIDE-SALT MELTS

A. P. Osokin¹ and E. N. Potapova¹Translated from *Steklo i Keramika*, No. 9, pp. 44–50, September, 2003.

The structure and properties of high-basicity aluminoferosilicate melts in the presence of individual and complex additives are investigated. The obtained regularities of modification of viscosity, surface tension, and structure of clinker liquid depending on the type and concentration of modifiers can be used to predict kinetics of liquid-phase sintering in different silicate systems.

Complex salt-oxide melts are formed in synthesis of various glass ceramic materials. The rate of mineral formation, phase composition, and microstructure of materials obtained in technology of glass, glass ceramics, binders and products of high-temperature slag processing depend on the structure and properties of aluminoferosilicate melts originating in firing. The structure and properties of melts based on acid and low-basicity systems are considered in detail in [1], but similar data for the high-basicity range of the $\text{CaO} - \text{SiO}_2 - \text{Al}_2\text{O}_3 - \text{Fe}_2\text{O}_3$ system with a calcium oxide content over 50% (here and elsewhere mass content is indicated) are virtually absent, which prevents predicting the mechanism and kinetics of mineral-forming reactions. Controlling the properties of high-basicity melts by optimizing the ratio between initial oxides is little effective [2, 3], and a cardinal modification is possible only in the case of using components that have a significant effect on the structure of the liquid phase.

At a temperature of 1338°C, a eutectic melt of the following composition emerges in the $\text{CaO} - \text{SiO}_2 - \text{Al}_2\text{O}_3 - \text{Fe}_2\text{O}_3$ system (%): 54.8 CaO, 6.0 SiO₂, 22.7 Al₂O₃, and 16.6 Fe₂O₃. On further temperature increase, the melt becomes saturated with oxides of calcium, silicon, aluminum, and iron, and at 1450°C it has the following composition (%): 57.0 CaO, 7.5 SiO₂, 22.6 Al₂O₃, and 12.9 Fe₂O₃.

The skeleton structure of a high-basicity aluminoferosilicate melt, according to IR spectroscopy data, is made up by silicon-oxygen radicals present mostly in the form of anions $[\text{SiO}_4]^{4-}$, ions Ca^{2+} , and amphoteric ions of aluminum which, depending on specific conditions, form part of groups $[\text{MeO}_4]^{5-}$ or $[\text{MeO}_6]^{9-}$. A salt-oxide melt typically forms

more complex groups of the type $\text{R}_1[\text{MeO}_4]^+$ or $\text{R}_2[\text{MeO}_4]^{2+}$ (R are weakly polarizing cations K^+ , Na^+ , etc.). The stronger cations (Mg^{2+}) are arranged near the non-bridge oxygen ions of the tetrahedron $[\text{SiO}_4]^{4-}$. With a low concentration of modifier ions, simple groups $[\text{MeO}_4]^{5-}$ or $[\text{MeO}_6]^{9-}$ prevail in the melt, which is corroborated by the IR spectra of respective melts. The amphoteric nature of aluminum and iron ions determines the existence of acid-base equilibrium between their different coordination forms in the melt:



The direction of a shift in acid-base equilibrium in a melt in the presence of modifying additives is determined by their acid-base properties. With a high content of modifiers, modifications of the properties of the liquid phase cannot be accounted for only in the context of acid-base equilibrium. The tendency of ions to associate with complex groups, on the one hand, and limited solubility of salts or salt-based complexes in an oxide melt, on the other hand, produce liquation phenomena, which modifies the melt structure and, accordingly, its properties, such as viscosity and surface tension.

In a joint presence of several ions in the liquid phase, its properties do not change additively depending on their concentration. To determine a complex effect of elements on the properties of the liquid phase, the mathematical design of experiment was used. The viscosity of melts was measured with a ÉVI-70 PM rotation electroviscometer, and the surface tension by the method of maximum pressure in a gas bubble. The choice of structure modifiers was based on the efficiency of their modification of the parameters of acid and low-basicity silicate melts [4].

¹ D. I. Mendeleev Russian Chemical Engineering University, Moscow, Russia.

Investigations revealed that alkali metal sulfates increase the mobility of the melt (Fig. 1, curves 1 and 3), but less intensely than only SO_4^{2-} anion. This is due to inter-ionic interactions in the melt, which leads to a modification of the acid-base equilibrium under a simultaneous effect of the acid (SO_4^{2-}) and the base (R^+) components. A less perceptible effect of K_2SO_4 compared to that of Na_2SO_4 , as well as abnormal behavior of the melt viscosity in the presence of K^+ and SO_4^{2-} is due to higher basicity of K^+ ion than that of Na^+ ion. As a consequence, the anion SO_4^{2-} does not compensate for equilibrium modification, and the viscosity of the melt with a content of K_2SO_4 over 1% increases. With a lower content of sulfates, their effect is registered to be additive. Magnesium oxides introduced in an amount up to 4% into the liquid phase decreases its viscosity. The cation Mg^{2+} has an especially intense effect when its content is up to 1%, which is due to lowering the strength of heterocomplexes.

The joint effect of alkali, magnesium, and sulfur oxides on the viscous flow of a high-basicity aluminoferosilicate melt differs depending on the ratio between the elements. An optimum ratio of $\text{R}_2\text{O} : \text{SO}_3 : \text{MgO}$ is 1 : 8 : 11 [5]. An introduction of the complex in an amount from 0.5 to 2.5% causes a significant decrease in the liquid phase viscosity, from, 0.08 Pa · sec (for initial melt) to 0.01 Pa · sec (the content of the complex 2.5%). A further increase in the concentration of this additive in the melt produces an insignificant decrease in viscosity.

If the ratio of R^+ , Mg^{2+} , and SO_4^{2-} ions in the melt is not controlled, they can form salt eutectics $\text{K}_2\text{SO}_4 \cdot 2\text{MgSO}_4$ (melting point 634°C), Na_2SO_4 (642°C) and $\text{K}_2\text{SO}_4 + \text{Na}_2\text{SO}_4 + \text{MgSO}_4$ (660°C) [6] and significantly modify the viscous flow of the melt (Fig. 1, curves 2 and 4). With a content of the double salt $\text{K}_2\text{SO}_4 \cdot 2\text{MgSO}_4$ in the liquid phase equal to 0.5 – 2.0%, the viscosity of the melt increases, and when this content is over 2%, the viscosity decreases. A certain increase in viscosity at low concentrations of the double salt can be interpreted in the context of acid-base equilibrium. When $\text{K}_2\text{SO}_4 \cdot 2\text{MgSO}_4$ in the melt dissociates into K^+ , Mg^{2+} , and SO_4^{2-} ions, potassium cations due to their higher basicity cause a shift in equilibrium toward the formation of an additional quantity of aluminum and iron ions in the tetrahedral coordination, which have decreased mobility. As a consequence, a slight increase in viscosity is registered.

The sodium double salt $\text{Na}_2\text{SO}_4 \cdot 3\text{MgSO}_4$ and the eutectic mixture of sulfates $\text{K}_2\text{SO}_4 + \text{Na}_2\text{SO}_4 + \text{MgSO}_4$ typically decrease the melt viscosity. In general, the introduction of potassium, sodium, and magnesium sulfates into the melt causes an intense decrease in viscosity with an increasing concentration of R_2SO_4 . To obtain preset values of the liquid phase viscosity, it is necessary to strictly observe an optimum combination of double salt element found in the mathematical design. Otherwise, liquation may take place, which can delay the process of mineral formation in synthesis of clinkers.

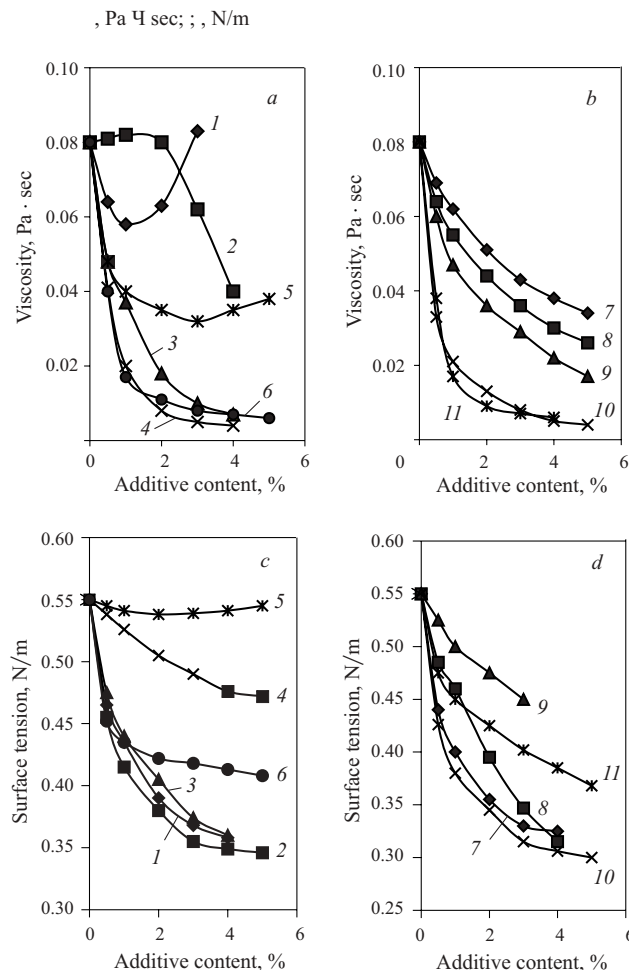


Fig. 1. Viscosity (a, b) and surface tension (c, d) isotherms of eutectic melt in the presence of additives (temperature 1450°C): 1) K_2SO_4 ; 2) $\text{K}_2\text{SO}_4 \cdot 2\text{MgSO}_4$; 3) Na_2SO_4 ; 4) $\text{Na}_2\text{SO}_4 \cdot 3\text{MgSO}_4$; 5) MgO ; 6) $\text{R}_2\text{O} + \text{MgO} + \text{SO}_3$; 7) CaSO_4 ; 8) CaCl_2 ; 9) CaF_2 ; 10) $\text{CaCl}_2 + \text{CaSO}_4$; 11) $\text{CaF}_2 + \text{CaSO}_4$.

The mobility of a high-basicity aluminoferosilicate melt grows in the presence of *p*-elements. (Fig. 1b). The viscosity decreases especially intensely in the presence of eutectic salt systems, whose compositions are listed in Table 1.

It follows from the results obtained (Fig. 1b) that complex salt additives are more effective than individual salts, and the intensity of their effect is even higher than the effect of halides, especially perceptible with a content up to 1%. The highest effect under a low content (up to 1.5%) was exercised by the additive $\text{CaF}_2 + \text{CaCl}_2$. When the content of

TABLE 1

Eutectic	$\text{CaF}_2 + \text{CaSO}_4$ (951°C)*	$\text{CaF}_2 + \text{CaCl}_2$ (651°C)	$\text{CaCl}_2 + \text{CaSO}_4$ (708°C)
CaF_2	50	19.5	—
CaCl_2	—	80.5	87.5
CaSO_4	50	—	12.5

* Melting point indicated in brackets.

these compositions grew to 5%, the minimum viscosity value (0.003 Pa · sec) was registered in a melt modified by the fluoride-sulfate mixture. The melts containing $\text{CaCl}_2 + \text{CaSO}_4$ in an amount of 3 – 5% had low viscosity values, which varied in the limits of 0.007 – 0.010 Pa · sec, which is presumably due to a predominant effect of Cl^- on the structure of melts containing F^- and SO_4^{2-} .

Thus, experimentally discovered acid-base interaction between various coordination forms between various coordination forms of aluminum and iron ions in salt-oxide melts has a critical effect on the parameters of their viscous flow, which is established both for individual salts and for some most effective mixtures. For some elements, such as Mg, a significant factor as well is a decreased energy of Ca – O bond in the presence of a stronger cation, whereas for other elements (F, Cl) an important factor is the screening capacity of the ion. Some mixtures exhibited an abnormal deviation from additivity, which was due to the mutual effect of ions introduced. Therefore, in selecting composition of complex catalysts, one should take into account not only modification of the acid-base properties of the melt, but also more complex inter-ionic interactions in the liquid phase.

The surface tension of melt is determined by the volume structure of liquid and mainly by the state of its surface layer. Therefore, surface tension upon introducing various elements can vary not only as a consequence of modified surface activity of matrix ions, but also due to high adsorption capacity of ions introduced. The regularities of surface tension variations in the melt depending on reactions between particles in its volume, the composition and structure of the surface layer, and on the type of modifying elements are observed less accurately, therefore in this case one can talk only of a trend in manifestation of the following regularities: surface tension decreases with growing basicity of *s*-elements and growing acidity of *p*- and *d*-elements.

The surface tension of a eutectic melt at a temperature of 1540°C is 0.55 N/m and decreases in the presence of sulfates of alkali metals (Fig. 1c). Its value with 3% Na_2SO_4 additive was 0.374 N/m, and with 3% K_2SO_4 it was 0.356 N/m. A different effect of sodium and potassium sulfates on the surface tension of the melt is due to a different value of energy of the bond of the cation to oxygen. A lower value of the bond energy for K – O (46 kJ · Avogadro number), than for Na – O (84 kJ · Avogadro number) determines lower surface tension of potassium-bearing melts. According to the regularities earlier obtained [7], low values of surface tension of melts containing alkali metal sulfates point to deterioration of the process of particle aggregation in the sintering zone of a rotating furnace, due to which a content of dust-like grains increases. Therefore, it is necessary to select complex additive compositions in such a way that their introduction would intensely lower the viscosity of the melt and insignificantly modify the surface tension.

One of additives, whose presence changes surface tension insignificantly, is magnesium oxide. The Mg^{2+} ion due

to its higher polarizing capacity than that of Ca^{2+} ion (the bond energy Mg – O is 163 kJ · Avogadro number) decrease the energy of Ca – O bond, which facilitates its easier rupture. As a consequence, silicon-oxygen complexes, which are weakly bonded in the melt, become additionally displaced to the surface layer and reduce the surface tension by diminishing the number of saturated bonds per surface unit of the melt.

In joint presence of R_2O , MgO , and SO_3 ($\text{R}_2\text{O} : \text{MgO} : \text{SO}_3 = 1 : 8 : 11$) the surface tension of the melt decreases to a lesser extent (Fig. 1, curve 6) than when the melt is modified by alkali metal sulfates. In this case the magnesium ion increases the solubility of alkali metal sulfates in the melt and thus prevents displacement of Na^+ and K^+ into the surface layers of the melt, accordingly, sulfate ions make the main contribution to decreasing the surface tension. This is corroborated by an intense decrease in surface tension in the presence of $\text{K}_2\text{SO}_4 \cdot 2\text{MgSO}_4$ and a eutectic mixture of sodium, potassium, and magnesium sulfates. The most perceptible decrease in surface tension is observed in the presence of complex additives introduced in an amount up to 2%.

A more intense decrease in the surface tension of the melt is observed in the presence of CaCl_2 (Fig. 1d). Enrichment of the surface layer of the melt with chloride ions raises the acidity of liquid contacting with CaO and $2\text{CaO} \cdot \text{SiO}_2$ particles, as a consequence of which a content of MeO_6 groups increases at the expense of MeO_4 , which facilitates a decrease in viscosity even compared to volume values found in measurements. The diffusion of Ca^{2+} and SO_4^{2-} ion intensifies in the emerging highly mobile melt layer, which activates the processes of dissolution and crystallization. A higher surface activity of Cl^- is due to a higher concentration of F^- ions than Cl^- ion in the coordination sphere of Ca^{2+} , which impedes their displacement into the surface layer of the melt. Furthermore, the radius of Cl^- (1.81 Å) exceeds the radius of F^- (1.33 Å), therefore, when O^{2-} ions in the surface layer are replaced by Cl^- , the surface energy of the melt and the surface tension decrease to a greater extent.

On introducing salt additives $\text{CaCl}_2 + \text{CaSO}_4$ and $\text{CaF}_2 + \text{CaCl}_2$, surface tension decreases more intensely than in the case of introducing individual salts, and the modifier $\text{CaF}_2 + \text{CaSiO}_4$ exhibits an additive effect of dissolved ions (Fig. 1, curves 10 and 11). The emerging melts are characterized by low surface energy, and the surface tension values with a 3 – 4% content of additives vary within the limits of 0.31 – 0.36 N/m, which is significantly lower than the surface tension of the initial melt (0.55 N/m). Based on intensity of lowering surface tension, the salt melts are ranked as follows: $\text{CaF}_2 + \text{CaSO}_4 \rightarrow \text{CaF}_2 + \text{CaCl}_2 \rightarrow \text{CaCl}_2 + \text{CaSO}_4$.

Liquation phenomena in acid silicate melt and glasses are thoroughly investigated [8, 9]. The stratification process is usually attributed to the propensity of cations for association with complex groups. The melt in liquation forms two liquid phases: a high-silica and a high-calcium phase, which

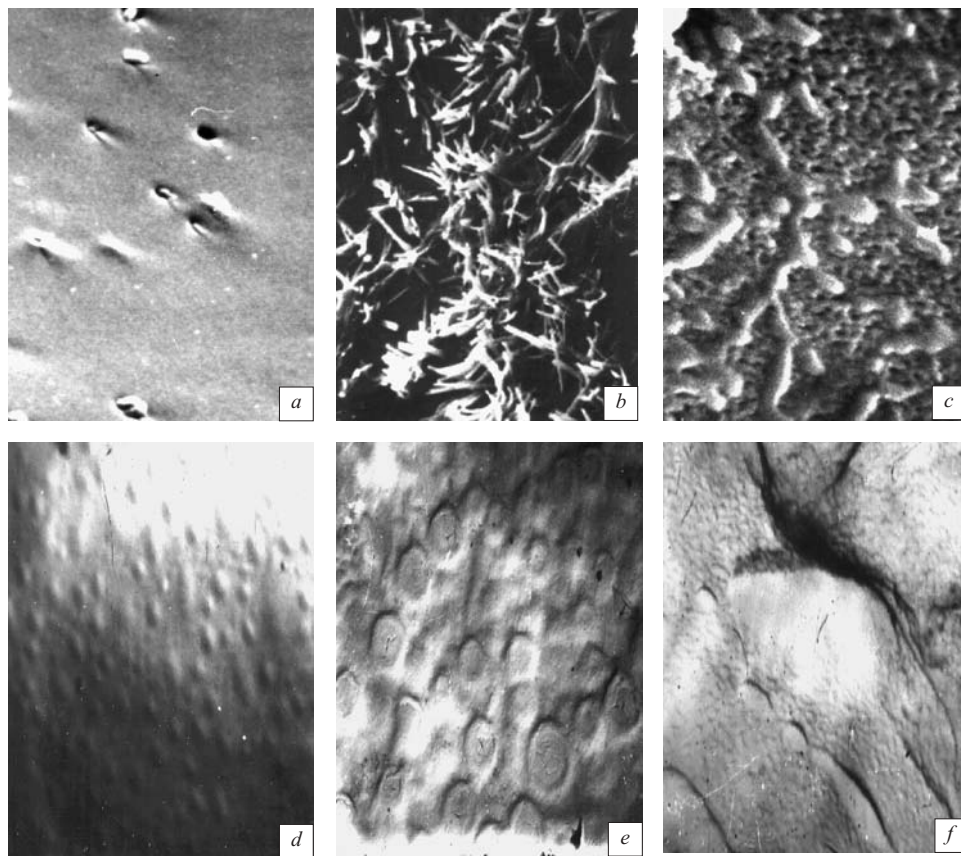


Fig. 2. Microstructure of clinker glass ($\times 10,000$) obtained by abrupt cooling of melts containing: *a*) 1% Na_2SO_4 ; *b*) 4% Na_2SO_4 ; *c*) 2% $\text{K}_2\text{SO}_4 \cdot 2\text{MgSO}_4$; *d*) 1% F^- ; *e*) 1% $(\text{CaF}_2 + \text{CaSO}_4)$; *f*) 1% $(\text{CaF}_2 + \text{CaCl}_2)$.

have different structure and properties [8]. Dissolving in the high-calcium strongly depolymerized phase, aluminato complexes raise its degree of polymerization and thus bring it closer to the structure and properties of the high-silica phase. As a consequence, the mutual solubility of two phases increases and the liquation temperature decreases. The tendency of melts for stratification well correlates with the value of their interphase surface energy. In the sequence of melts $\text{Li}_2\text{O} + \text{SiO}_2$, $\text{Na}_2\text{O} + \text{SiO}_2$ and $\text{K}_2\text{O} + \text{SiO}_2$ the interphase energy decreases from Li to K and the mean size of the disperse phase particles decreases in the same order due to the prevalence of the entropy factor and the range of metastable liquation becomes narrower [9]. Adding a third component (oxide) to binary liquating melts results in its distribution between the coexistent phases. In the presence of an oxide containing a weaker cation, liquation phenomena in the melt with a stronger cation decrease.

The considered regularities of liquation phenomena are preserved in high-basicity aluminosilicate melts, although an increased content of cations in the latter is responsible for some anomalies. The formation of micro- and macro-liquation salt zones differing in their acid-base properties is related to different mobility of ions in the melt and high surface activity of cations and *p*-element ions. In

the presence of alkali metal sulfates, oxide liquid is immiscible with the salt melt (Fig. 2*a* and *b*) and the degree of their mutual solubility varies depending on the type and content of salt introduced. Differentiation of the liquid phase composition occurs due to adsorption of anion groups in the surface layer of the melt, and due to low mobility of silicon-oxygen complexes, which causes their increased concentration in the melt zones adjacent to dissolving silica-bearing phases. With a sulfate content ranging from 0.5 to 0.8%, they completely dissolve in the oxide matrix, and after melt hardening, a sufficiently homogenous vitreous phase is formed with occasional inclusions of crystals $3\text{CaO} \cdot \text{Al}_2\text{O}_3$. When the content of R_2SO_4 is over 1%, microliquation is observed (Fig. 1*a*). The size of liquation zones in systems with Na_2SO_4 and K_2SO_4 is different.

It is demonstrated in [8] that there is a clear correlation between the liquation zone width and the cation parameters. A potassium-bearing melt has less surface energy than a melt with Na^+ . Therefore, due to the prevalence of the entropy factors, the average particles size will diminish in transition $\text{Na} \rightarrow \text{K}$ and the metastable liquation range will become narrower. The liquation drop size in a melt containing 1% K_2SO_4 is equal to $(0.6 - 1.3) \times 10^3 \text{ \AA}$, whereas in a melt containing 1% Na_2SO_4 the average drop size is $(1 - 3) \times 10^3 \text{ \AA}$.

TABLE 2

Melt modifier	Mass content, %								
	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	SO ₃	K ₂ O	Na ₂ O	C ₃ S
K ₂ SO ₄	5.95	1.40	0.08	0.01	—	42.56	50.00	—	4.67
Na ₂ SO ₄	5.90	1.30	0.08	0.01	—	52.23	—	40.28	4.35
K ₂ SO ₄ · 2MgSO ₄	13.78	1.93	0.46	1.09	3.88	56.49	21.30	1.07	6.43
Na ₂ SO ₄ + K ₂ SO ₄ + MgSO ₄	13.49	2.16	0.22	0.19	1.44	56.60	13.60	15.50	7.20
Na ₂ SO ₄ · 3MgSO ₄	13.52	2.31	0.29	0.31	4.37	66.35	0.61	12.24	7.70

With 2% K₂SO₄ the liquation areas grow, single drops merge and form a worm-shaped lattice structure. When modifiers are introduced above 3%, the oxide melt matrix cannot retain large areas of salt melts, they start migrating toward the surface layers and due to a decreased density ($\rho_{\text{K}_2\text{SO}_4} = 1.82 \text{ g/cm}^3$, $\rho_{\text{Na}_2\text{SO}_4} = 1.93 \text{ g/cm}^3$, $\rho_{\text{melt}} = 2.8 \text{ g/cm}^3$), the salt phase forms a surface layer on top of the oxide melt. Macroliquation is a kinetic process and in the case of macrostratification, drops of sulfate-alkali melts are present in the oxide melt volume and crystallize in the case of sharp cooling (Fig. 2b).

On introducing a third component (for instance MgO) into a liquating sulfate-alkali system, the oxide is distributed between the existent phases and, as a consequence of increasing the surface energy of the oxide melt, the solubility of alkali sulfates in this melt grows, which weakens the liquation phenomena. This regularity is observed both in introducing Mg²⁺ ions into a melt containing the complex R₂O + SO₃, and in adding double salts Na₂SO₄ · 3MgSO₄ and K₂SO₄ · 2MgSO₄. A high concentration of magnesium ions completely suppresses liquation.

An intense decrease in viscosity and surface tension is observed in the presence of the complex R₂O + MgO + SO₃ up to 2%, and with a higher content, microliquation starts and the melt properties virtually do not change. When a content of SO₄²⁻ in a melt containing R⁺ and Mg²⁺ increases, K₂SO₄ · 2MgSO₄, K₂SO₄ + Na₂SO₄ + MgSO₄, and Na₂SO₄ · 3MgSO₄ are formed, and the melt structure in their presence significantly changes. With more than 1.0% Na₂SO₄ · 3MgSO₄ and more than 1.5% K₂SO₄ · 2MgSO₄, microliquation is observed, which transforms into macroliquation, as their respective contents grow to 1.5 and 2.0%. The low surface tension of the melt (0.42 N/m) in the presence of Na₂SO₄ facilitates the displacement of the sodium-magnesium-sulfate liquid into the surface layer. Decreased solubility of NaSO₄ · 3MgSO₄ in an oxide melt leads to the crystallization of the liquating phases in cooling in the form of needles. As the content of the modifier grows to 3.0%, single needles form long fibers. With 2% K₂SO₄ · 2MgSO₄, the structure of an abruptly chilled melt is represented by spongy clusters of different shapes and sizes (Fig. 2c). An increase in the additive content up to 3% facilitates merging of these clusters.

Liquation phenomena in halogen-bearing melts are observed under lower concentrations of anions than in sulfate

melts. The emergence of liquation areas in silicate halogen-bearing melts and glasses is interpreted [1] in the context of the screening theory developed by Veile. According to this theory, the degree of screening of cations grows with increasing polarizability capacity of cations. Since ion F⁻ has a lower value of polarizability [0.96 (Å)³] than the oxygen ion [2.74 (Å)³], it completely dissolves in the oxide melt and as the content of fluoride ions further increases, liquation zones of size (2–3) × 10³ Å are formed. Cl⁻ ions are characterized by higher polarizability than F⁻ ion, therefore, in its presence the degree of screening grows, microliquation arises at a higher content of Cl⁻ (2–3%) and is accompanied by the formation of liquation areas of smaller sizes.

On introducing eutectic salt mixtures, microliquation in a melt arises at a lower absolute concentration of *p*-elements with formation of larger zones. The size of liquation areas in replacing CaCl₂ by CaSO₄ in a fluorine-containing melt grows from (0.5–1.0) × 10³ to (6–12) × 10³ Å (Fig. 2, *d–g*). In halogen-bearing melts immiscibility is typically observed even in the absence of alkali cations, and after introduction of complex salts, their concentration decreases virtually by half and determines the formation of salt melts. Therefore, with a total content of fluoride, chloride and sulfate equal to 0.3–0.5%, one should expect the formation of microliquation zones in the oxide melt.

The mutual solubility of components of oxide and salt melts was identified by the method of isothermic saturation of macroliquating phases with subsequent abrupt cooling of melts and determination of the composition of the oxide glass and the liquating phase. The solubility of salt melts in an oxide melt at a temperature of 1450°C does not exceed 3–5%, and at higher concentrations, micro- and then macro-liquation start. The solubility of oxides (especially CaO) varies significantly depending on the temperature and composition of the liquating phase. Salt melts based on R₂SO₄ dissolve 5.90–5.95% CaO and 1.3–1.4% SiO₂, whereas aluminum and iron oxides are virtually insoluble (Table 2). The content of CaO in melts based on Na₂SO₄ + K₂SO₄ + MgSO₄, Na₂SO₄ · 3MgSO₄, and K₂SO₄ · 2MgSO₄ is 13.49–13.78%, the content of SiO₂ in these melts grows to 1.93–2.31%, and Al₂O₃ and Fe₂O₃ dissolve in an amount of 0.19–1.09%.

High solubility of CaO in sulfate-magnesium melts is due to the formation of intermediate compounds of the type of K₂SO₄ · CaSO₄ · MgSO₄ and K₂SO₄ · 2CaSO₄. The process of dissolution of calcium oxide occurs through ionic ex-

change $\text{Mg}^{2+} \leftrightarrow \text{Ca}^{2+}$ on the CaO – salt met interface. The proximity of the energy and geometrical parameters of these cations facilitates the dissolution process. An exchange of Na^+ and K^+ ions with Ca^{2+} is difficult due to a difference in their charges, which lowers the concentration of CaO in R_2SO_4 melts. Silicon, aluminum, and iron ions do not have isomorphic anions in salt melts, therefore, their concentrations are not high.

The solubility of CaO in complex salt melts based on $\text{CaF}_2 + \text{CaCl}_2$, $\text{CaF}_2 + \text{CaSO}_4$, and $\text{CaCl}_2 + \text{CaSO}_4$ increases with increasing temperature in an interval of $950 - 1320^\circ\text{C}$ (temperature coefficient $2 \times 10^{-2} \text{ }^\circ\text{C}^{-1}$). The maximum solubility of CaO (12 – 15%) at a temperature of $1100 - 1300^\circ\text{C}$ is observed in the salt melt based on $\text{CaCl}_2 + \text{CaSO}_4$ and its values decrease in a consecutive replacement of anions in the sequence of $\text{Cl}^- \rightarrow \text{F}^- \rightarrow \text{SO}_4^{2-}$. All melts investigated exhibit rather high dissolution of CaO at relatively low temperatures, accordingly, by extrapolating the regularities obtained to a temperature of 1450°C , we can assume that the ultimate solubility of CaO will significantly exceed the respective values determined for mixtures of alkali metal sulfates. Multicomponent salt melts saturated with CaO can dissolve up to 1.83% SiO_2 (at 900°C , mixture $\text{CaF}_2 + \text{CaCl}_2$) and up to 1% aluminum and iron oxides.

CaO dissolves more intensely in highly mobile salt melts, and these melts act as a transport medium for calcium cations diffusing into local areas rich in silica-bearing components, where the formation and crystallization of tricalcium silicate takes place. In crystallization of salt melts saturated with calcium, aluminum, and iron oxides, in which liquation is observed, along with single or double salts there are silicate phases, predominantly C_3S . According to the chemical analysis data of an extract in boric acid, 4 – 5% calcium silicate is formed in melts of alkali metal sulfates. Excessive calcium oxide forms CaSO_4 and $\text{R}_2\text{SO}_4 \cdot \text{CaSO}_4$ and also dissolves in the sulfate, which causes a shift in the absorption bands in the IR spectrum of Na_2SO_4 : $615, 640 \rightarrow 625, 645$ and $1120 \rightarrow 1090 \text{ cm}^{-1}$. In the presence of Mg^{2+} , double salts are formed: $\text{K}_2\text{SO}_4 \cdot 2\text{MgSO}_4$ (4.05, 3.14, 2.65 Å), $\text{K}_2\text{SO}_4 \cdot \text{CaSO}_4 \cdot \text{MgSO}_4$ (4.15, 3.21, 2.74 Å), and the content of calcium silicates grows (to 6.5%), which, however, cannot be identified by x-ray phase analysis, since their diffraction reflections are superimposed on the peaks of the prevailing phase $\text{K}_2\text{SO}_4 \cdot 2\text{MgSO}_4$. The emergence of absorption bands at 490 and 835 cm^{-1} typical of C_3S corroborates its crystallization from the melt.

Similar studies performed with halogen-bearing salt melts saturated with aluminum, silicon, iron, and calcium oxides also corroborated the formation of calcium silicates. In cooling of salt melts, 6 – 9% tricalcium silicate crystallizes.

Thus, the studies performed revealed a modification of the structure and properties of high-basicity aluminosilicate melts in the presence of individual and mixed additives containing halides and sulfates of alkali metals. The structure of modified melts depends on the acid-base proper-

ties of dissolving ions and the effect of the modifiers depends on the direction of the shift of acid-base equilibrium in the melt.

It is established that a high-basicity melt in the presence of salts and their mixtures stratifies into two liquid phases: an oxide phase with dissolved ions of the salt introduced and a salt phase containing ions of the oxide component. The propensity of a melt for liquation increases with growing acidity of anions introduced in the series $\text{SO}_4^{2-} \rightarrow \text{Cl}^- \rightarrow \text{F}^-$ and with increasing basicity of s -elements in the series $\text{Mg}^{2+} \rightarrow \text{Na}^+ \rightarrow \text{K}^+$, which correlates with the modification of the surface energy of the melt and in general agrees with the regularities revealed for more acid systems. Calcium oxide is most dissolving component in high-mobility salt melts, whereas the concentration of aluminum, silicon, and iron ions is not high.

The regularities obtained on modifications of viscosity, surface tension, and structure of clinker liquid depending on the type and concentration of modifiers can be used in predicting kinetics of liquid-phase sintering for various silicate systems.

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